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GENERATION AND [2+3] CYCLOADDITIONS OF A SULFONYLATED THIOCARBONYL *S*-METHANIDE

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Abstract – The sulfonylated thiocarbonyl *S*-methanide (**2a**) was generated *in situ* by addition of diazomethane to the *C*-sulfonylated dithioformate (**1a**) and subsequent thermal elimination of nitrogen. This 1,3-dipole was intercepted by C,C- and C,S-dipolarophiles. Whereas in the first case the cycloadducts (**10**) and (**11**) could be isolated as stable products, the cycloadducts of type (**8**), which are the proposed products of the reaction with thioketones, underwent a spontaneous rearrangement to give open-chain ketene dithioacetals (**5**) and (**6**).

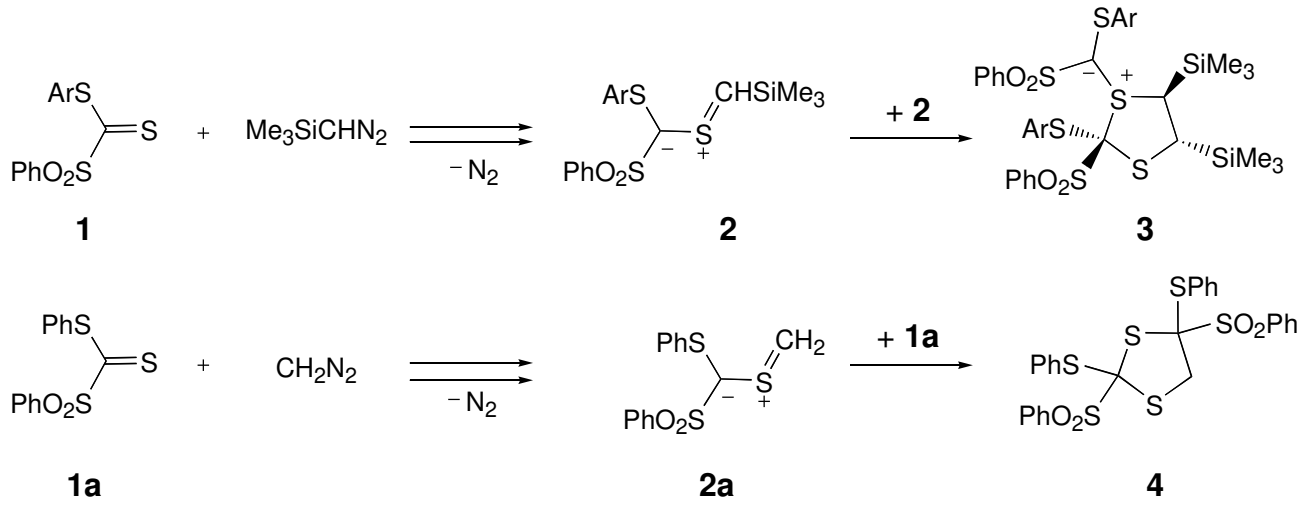
INTRODUCTION

C-Sulfonylated dithioformates (**1**) are versatile thiocarbonyl reagents, which show high reactivity towards electrophiles, nucleophiles and dienes.[2] It can be expected that, in comparison with other dithioesters, the presence of the sulfonyl group also enhances the dipolarophilicity of these relatively easily available compounds. However, there are only a few reports on their [2+3] cycloadditions.

It is well established that thiocarbonyl compounds can be used as convenient precursors of reactive thiocarbonyl *S*-methanides *via* initial addition of diazomethane and subsequent thermal elimination of nitrogen.[3] In a recent paper, *Senning* and coworkers reported on an unexpected dimerization of a thiocarbonyl *S*-methanide (**2**), which was generated by treatment of an aryl *C*-

(phenylsulfonyl)dithioformate (**1**) with trimethylsilyl diazomethane.[4] The reaction was carried out in pentane in the absence of any intercepting reagent, and the structure of the dimer was established as the sulfur ylide (**3**) by X-Ray crystallography (*Scheme 1*).

Scheme 1



In an earlier report, the treatment of **1a** with diazomethane at room temperature to give dithiolane (**4**) was described.[5] Based on present knowledge, both reactions are believed to occur *via* reactive thiocarbonyl *S*-methanides of type (**2**). Analogous reactions, which were carried out with phenyl- and diphenyldiazomethane, yielded the corresponding thiiranes *via* 1,3-dipolar electrocyclization of the intermediate thiocarbonyl S-ylides.[5]

To the best of our knowledge, there are no reports describing attempts to intercept sulfonylated thiocarbonyl *S*-methanides of type (**2**) with dipolarophiles. Due to our ongoing interest in the exploration of reactive thiocarbonyl *S*-methanides for the synthesis of functionalized *S*-heterocycles, we investigated phosphonylated[6] and sulfonylated dithioformates as new precursors of these species. In the present paper, we describe the results obtained by using the sulfonylated dithioformate (**1a**).

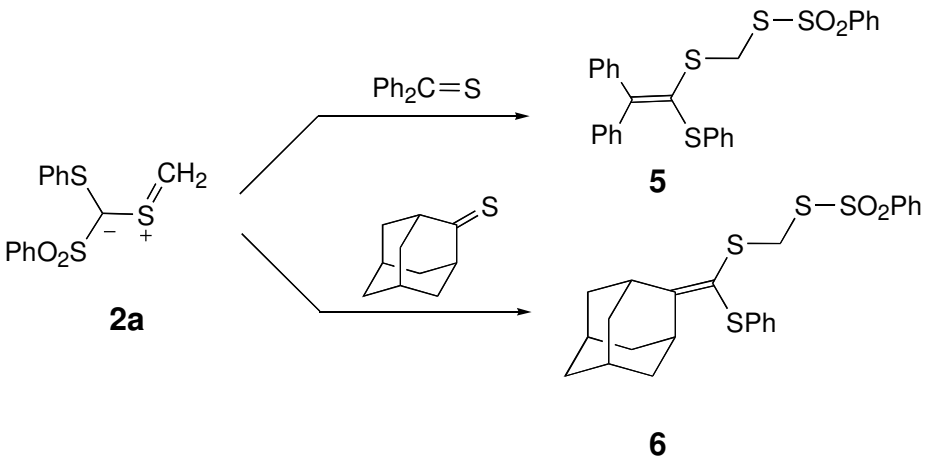
RESULTS AND DISCUSSION

The repeated experiment with phenyl *C*-(phenylsulfonyl)dithioformate (**1a**) and diazomethane at 0°C led to a solid product in low yield (ca. 5%), which, according to the ^{1}H-NMR spectrum, was identical with **4**.[5] In order to test if the intermediate (**2a**) undergoes a 1,3-dipolar electrocyclization to give the corresponding thiirane, or if a cyclodimerization occurs, analogous

to the reaction in *Scheme 1*, **1a** was treated with diazomethane at –60°C until the red color of the solution disappeared. After warming to –30°C, evolution of nitrogen was observed, but no product could be isolated by means of crystallization nor by chromatographic workup.

As thiobenzophenone is known as a 'superdipolarophile',[7] which efficiently traps both aromatic and aliphatic thiocarbonyl *S*-methanides, it was selected as a trapping agent for **2a**. Addition of thiobenzophenone to a solution of the precursor of **2a**, prepared by addition of diazomethane to **1a** at –60°C, and subsequent warming to room temperature afforded a single product, which in the ^{1}H-NMR spectrum displayed unexpectedly a singlet at 4.25 ppm for CH_2. The expected 1,3-dithiolane should show an AB system in the region of 3-4 ppm. The ^{13}C-NMR spectrum of the isolated crystalline material (**5**) showed a signal for CH_2 at 38.9 ppm and six signals for quaternary C-atoms between 125.9 and 154.6 ppm. The MS spectrum (CI) confirmed the formation of a 1:1 adduct of thiobenzophenone and **2a**. The analogous reaction with the less reactive adamantanethione led to product (**6**) with signals for CH_2 at 4.37 (singlet) and 36.5 ppm (^{1}H and ^{13}C-NMR spectrum, respectively). The structure of **6** was unambiguously established by X-Ray crystallography (*Scheme 2, Figure 1*). By analogy, the structure of the product obtained in the reaction with thiobenzophenone was formulated as **5**.

Scheme 2



The isolated products, which correspond to ketene dithioacetals, are isomers of the expected 1,3-dithiolanes of type **7** and **8**, which could not be detected (^{1}H-NMR spectrum) in the reaction mixture. A rationalization of the reaction pathway is based on the assumption that the cycloaddition occurred regioselectively to give **8**, which rearranged by elimination of benzene sulfinate and subsequent ring opening according to *Scheme 3*. An analogous reaction mechanism has been proposed for the isomerization of the 1,3-dithiolane obtained from thio-

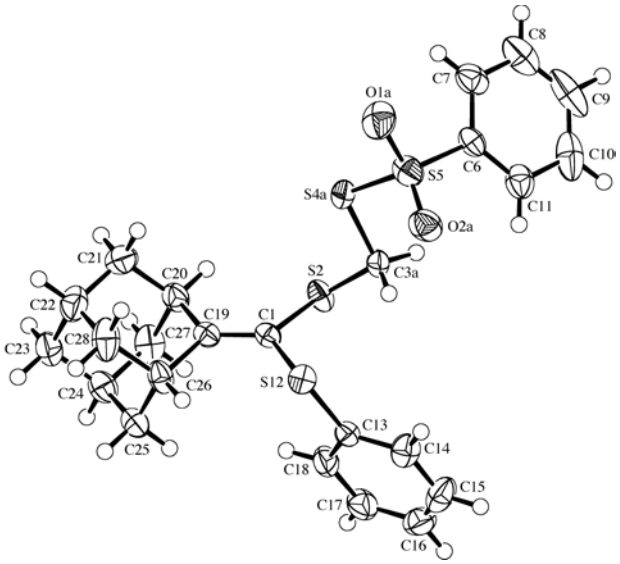
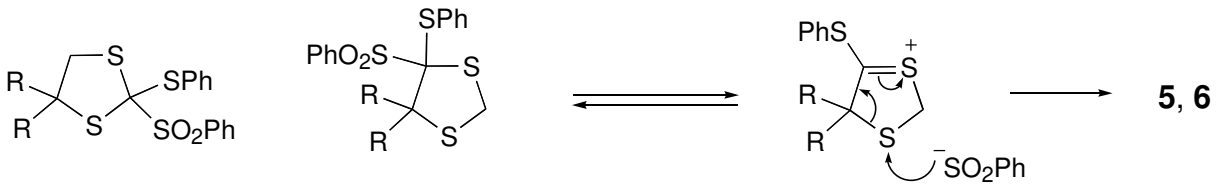


Figure 1. ORTEP plot[8] of the molecular structure of the major disordered conformation (86%) of **6** (arbitrary numbering of the atoms; 50% probability ellipsoids)

benzophenone *S*-methanide and diphenyl trithiocarbonate.[9] In the latter case, however, an acid (SiO_2 or TFA) was needed to catalyze the conversion. The present result confirms that benzene sulfinate is a better leaving group than thiophenolate.

Scheme 3



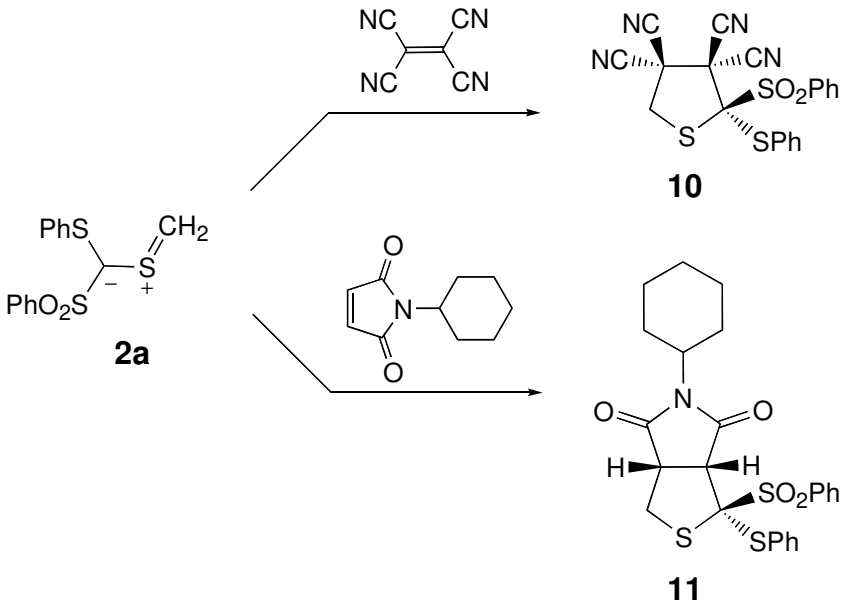
7 **8** **9**

In a 'reversed cycloaddition', *i.e.*, the reaction of thiobenzophenone *S*-methanide with **1a**, both 1,3-dithiolanes (**7**) and (**8**) were formed in a ratio of 1:9 according to the ^{1}H-NMR spectral analysis: in addition to the singlet at 4.25 ppm corresponding to the main product (**5**), which is formed by rearrangement of **8**, an AB system for CH_2 of **7** was present at 3.4-3.5 ppm. However, the attempted isolation of **7** failed. An analogous result was obtained when adamantanethione *S*-methanide was generated in the presence of **1a** (ratio of isomers *ca.* 1:9). In all reactions presented, the sterically more congested cycloadduct of type **8** was formed predominantly. This behavior is typical for *S*-methanides derived from aromatic thioketones and

has been rationalized by a stepwise mechanism via biradical intermediates.[10] Therefore, the results obtained with thiobenzophenone and thiobenzophenone *S*-methanide fit well with expectations. On the other hand, the clear preference for the formation of **8** in the case of adamantanethione and its *S*-methanide was unexpected and highlights the fact that the stabilization of the intermediate biradical by sulfur substituents is even more effective than in the case of aryl groups. For comparison, the cycloadditions of adamantanethione *S*-methanide with thiobenzophenone led to comparable amounts of the regioisomeric 1,3-dithiolanes.[11,12]

The efficient trapping of **2a** by thioketones prompted us to test C,C-dipolarophiles. Surprisingly, the attempted interception of **2a** with dimethyl acetylenedicarboxylate was unsuccessful. However, the highly reactive tetracyanoethene (TCNE) underwent a smooth [2+3] cycloaddition at –30°C to give the racemic tetrahydrothiophene (**10**) in 34% yield (*Scheme 4*). Similarly, the expected bicyclic cycloadduct (**11**) was obtained in 41% yield in the reaction of **2a** with *N*-cyclohexyl maleimide. In this case, the ^{1}H-NMR spectrum of the isolated solid revealed the presence of a 9:1 mixture of two diastereoisomers, which could not be separated by crystallization. In analogy to phosphonylated compounds, we propose that the larger $PhSO_2$ group of the major diastereoisomer is *exo* oriented.[6]

Scheme 4



In summary, the results described show that the sulfonylated dithioformate (**1a**) reacts easily with diazomethane at –60°C to give a 2,5-dihydro-1,3,4-thiadiazole, which decomposes at *ca.* –30°C to give the reactive thiocarbonyl *S*-methanide (**2a**). This intermediate undergoes [2+3]

cycloadditions with reactive C,C dipolarophiles to yield tetrahydrothiophene derivatives. The interception with thioketones is even more efficient and yields the sterically more crowded 1,3-dithiolanes (**8**) regioselectively. Under the reaction conditions, these proposed cycloadducts undergo a spontaneous rearrangement and ketene dithioacetals (**5**) and (**6**) are obtained as final products.

EXPERIMENTAL

General remarks. Melting points were determined in a capillary using a MEL-TEMP II apparatus (Aldrich) and are uncorrected. IR spectra were recorded with a FT-IR NEXUS instrument as KBr pellets, and the positions of the absorption bands are given in cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a TESLA BS 687 (^{1}H at 80 MHz, ^{13}C at 20 MHz) or BRUKER-AC-300 (^{1}H at 300 MHz, ^{13}C at 75 MHz) instrument in $CDCl_3$ solutions using TMS (δ = 0 ppm) as an internal standard; chemical shifts (δ) in ppm. MS spectra were recorded on a LKB-2091 spectrometer at 70 eV using electron impact (EI-MS) or chemical ionisation (CI-MS; with NH_3 or *i*-butane); *m/z* (rel.%). Elemental analyses were performed at analytical laboratories of the University of Zurich or at the Polish Academy of Sciences in Lodz. Tetrahydrofuran used as a solvent was freshly distilled over sodium ketyl prior to use.

Starting materials. Thiobenzophenone was prepared according to ref.[13] by heating commercial benzophenone with Lawesson's reagent in boiling toluene and purified by column chromatography over silica gel. Adamantanethione was generated from adamantanone and phosphorus pentasulfide by following a procedure by Greidanus.[14] The freshly prepared crude product was sufficiently pure for further applications. *S*-Phenyl *C*-benzenesulfonyldithioformate was prepared in a two-step procedure described by Senning, starting from thiophosgene and phenylsulfane.[15] *N*-Cyclohexylmaleimide was synthesized following a literature protocol.[16]

Reactions of 2a with thiobenzophenone, adamantanethione, tetracyanoethene and *N*-cyclohexyl maleimide. General procedure. A solution of **1a** (294.0 mg, 1 mmol) in dry THF (2 ml) under a N_2 atmosphere was placed in a flask equipped with a magnetic stirring bar. The red colored solution was cooled in an acetone/dry ice bath to –65ºC. While stirring, a solution of diazomethane in Et_2O was added drop-wise until the color of the starting material disappeared completely. Each drop of added solution caused stepwise decolorization of the reaction mixture. To the magnetically stirred colorless solution, 1 mmol of the corresponding dipolarophile was

added at –60ºC. Subsequently, the mixture was warmed slowly, and between –35ºC and –30ºC an intense evolution of N_2 was observed. Stirring was continued for 30 min and subsequently the cooling bath was removed allowing the mixture to warm slowly to rt (*ca.* 2 h). The solvent was evaporated and the crude reaction mixtures were analyzed by ^{1}H-NMR spectroscopy. Subsequent separation on preparative plates precoated with silica gel yielded pure products. Analytically pure samples were obtained by crystallization.

S-[(2,2-Diphenyl-1-phenylsulfanyl)vinylsulfanyl]methyl benzenethiosulfonate (**5**). Yield: 200 mg (40%). Colorless prisms (hexane/CH_2Cl_2); mp 121-123ºC. IR: 1316*m*, 1143*s*, 750*m*, 701*m*, 595*s*. ^{1}H-NMR: 4.25 (*s*, CH_2); 7.12-7.29 (*m*, 14 H_{arom}); 7.31-7.61 (*m*, 4 H_{arom}); 7.83-7.86 (*m*, 2 H_{arom}). ^{13}C-NMR: 38.9 (CH_2); 125.9 (C_q); 126.7, 127.0, 127.7, 127.8, 127.9, 128.1, 128.9, 129.1, 129.2, 129.4, 133.5 (20 CH_{arom}); 134.7 ($C_{q\text{-}arom}$); 141.0 ($C_{q\text{-}arom}$); 141.5 ($C_{q\text{-}arom}$); 144.7 (C_q); 154.6 ($C_{q\text{-}arom}$-SO_2). CI-MS (NH_3): 524 (27, [*M*+NH_4]$^+$), 365 (100), 333 (31), 268 (44). Anal. Calcd for $C_{27}H_{22}O_2S_4$: C, 64.00; H, 4.38; S, 25.31. Found: C, 63.92; H, 4.36; S, 25.69.

S-[(Adamantan-2-ylidene)(phenylsulfanyl)methylsulfanyl]methyl benzenethiosulfonate (**6**). Yield: 250 mg (53%). Colorless prisms (MeOH/CH_2Cl_2); mp 99-100ºC. IR: 2910*m*, 1321*m*, 1145*s*, 601*s*, 536*m*. ^{1}H-NMR: 1.65-1.93 (*m*, 12 H); 3.24, 3.53 (2*s*, 2 adamantan-H); 4.37 (*s*, CH_2); 7.12-7.28 (*m*, 5 H_{arom}); 7.50-7.67 (*m*, 3 H_{arom}); 7.90-7.93 (*m*, 2 H_{arom}). ^{13}C-NMR: 27.6, 37.0, 37.7 ($CH_{2\text{-}ad}$); 36.5 (CH_2); 39.1, 39.3, 39.5 ($CH_{2\text{-}ad}$); 111.4 (C_q); 125.9, 127.1, 127.8, 128.9, 129.1, 133.5 (10 CH_{arom}); 135.6 ($C_{q\text{-}arom}$); 144.9 (C_q); 169.8 ($C_{q\text{-}arom}$-SO_2). CI-MS (NH_3): 492 (16 [*M*+NH_4]$^+$), 333 (100). Anal. Calcd for $C_{24}H_{26}O_2S_4$: C, 60.72; H, 5.52; S, 27.02. Found: C, 60.66; H, 5.44; S, 27.17.

Suitable crystals for the X-Ray crystal-structure determination were grown from MeOH/CH_2Cl_2 by slow evaporation of the solvent.

2-Benzenesulfonyl-2-(phenylsulfanyl)tetrahydrothiophene-3,3,4,4-tetracarbonitrile (**10**). Yield: 150 mg (35%). Colorless crystals (hexane/CH_2Cl_2); mp 178-180^{o}C (decomp). IR: 3008*w*, 2999*w*, 2251*w* (C≡N), 1439*m*, 1328*m*, 1146*m*, 686*m*, 572*s*, 543*m*. ^{1}H-NMR: 3.75, 4.27 (*AB*, *J* = 12.5 Hz, CH_2); 7.28-7.34 (*m*, 4 H_{arom}); 7.45-7.51 (*m*, 1 H_{arom}); 7.71-7.76 (*m*, 2 H_{arom}); 7.89-7.93 (*m*, 1 H_{arom}); 8.28-8.30 (*m*, 2 H_{arom}). ^{13}C-NMR: 41.3 (CH_2); 49.7, 90.5 (2 C_q); 107.6, 107.7, 108.9, 110.2 (4 CN); 126.3 (C_q); 129.3, 129.4, 132.1, 133.1, 136.3, 137.2 (10 CH_{arom}); 132.5 (C_q); 156.0 ($C_{q\text{-}arom}$-SO_2). CI-MS (NH_3): 454 (79, [*M*+NH_4)$^+$]), 344 (29), 295(100), 296(18), 268 (35). Anal. Calcd for $C_{20}H_{12}N_4O_2S_3$: C, 55.03; H, 2.27; N, 12.83; S, 22.04. Found: C, 54.43; H,

2.69; N, 12.92; S, 21.71.

2-Benzenesulfonyl-7-cyclohexyl-2-phenylsulfanyl-3-thia-7-azabicyclo[3.3.0]octane-6,8-dione (**11**). Yield: 200 mg (41%). Colorless crystals (hexane/CH_2Cl_2); mp 104-106°C. IR: 2946*m*, 2923*m*, 1710*vs* (C=O), 1702*vs* (C=O), 1369*s*, 1295*s*, 1143*s*, 688*m*, 570*s*. ^{1}H-NMR: 1.14-2.25 (*m*, 10 $H_{c\text{-}hex}$); 3.32-3.76 (*m*, 3 H); 3.95-4.11 (*m*, 2 H); 7.16-7.78 (*m*, 8 H_{arom}); 8.17-8.20 (*m*, 2 H_{arom}). ^{13}C-NMR: 24.8, 25.6, 25.7, 28.6, 29.2 (5 $CH_{2\text{-}c\text{-}hex}$); 35.1 ($CH_2$-S); 52.5, 52.7 (2 CH); 54.3 (CH-N); 90.0 (C_q); 124.8, 128.3, 128.6, 129.0, 130.5, 131.9, 132.4, 134.5, 134.7, 137.7 (10 CH_{arom}), 128.7 ($C_{q\text{-}arom}$); 133.6 ($C_{q\text{-}arom}$-SO_2); 171.7, 176.5 (2 C=O). CI-MS (NH_3): 346 (20, [*M*-$C_6H_5SO_2$]$^+$), 271 (72), 268 (100), 160 (16). Anal. Calcd for $C_{24}H_{25}NO_4S_3$: C, 59.11; H 5.17; N 2.87; S 19.73. Found: C 58.73; H 5.16; N 2.82; S 19.48.

Reactions of thiocarbonyl *S*-methanides with 1a. The reactions of **1a** with thiobenzophenone *S*-methanide and adamantanethione *S*-methanide were performed according to the well-established procedures described in detail in recent papers, see *e.g.* refs.[6, 17]

X-Ray Crystal-Structure Determination of 6 (see *Table 1* and *Figures 1*).[18] All measurements were performed on a *Nonius KappaCCD* area-detector diffractometer[19] using graphite-monochromated MoK_a radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in *Table 1*, and a view of the molecule is shown in *Figure 1*. Data reduction for was performed with *HKL Denzo* and *Scalepack*.[20] The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method[21] was applied. The structure was solved by direct methods using SIR92,[22] which revealed the positions of all non-H-atoms. Atoms C(3), S(4), O(1) and O(2) are disordered. Two positions were defined for each of these atoms and refinement of the site occupation factors yielded a value of 0.856(2) for the major conformation. Bond length and similarity restraints were applied to all chemically equivalent bond lengths and angles involving the disordered atoms, while neighboring chain atoms within and between each disordered conformation were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent atom. The refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied.

Neutral atom scattering factors for non-H-atoms were taken from ref.[23a], and the scattering factors for H-atoms were taken from ref.[24] Anomalous dispersion effects were included in F_c;[25] the values for f' and f'' were those of ref.[23b] The values of the mass attenuation coefficients are those of ref.[23c] All calculations were performed using the SHELXL97 program.[26]

Table 1. *Crystallographic Data of Compound* (**6**)

Crystallized from	$MeOH/CH_2Cl_2$
Empirical formula	$C_{24}H_{26}O_2S_4$
Formula weight [g mol^{-1}]	474.71
Crystal color, habit	colorless, plate
Crystal dimensions [mm]	$0.15 \times 0.17 \times 0.25$
Temperature [K]	160(1)
Crystal system	monoclinic
Space group	$P2_1/c$
Z	4
Reflections for cell determination	25926
2θ range for cell determination [°]	$4-50$
Unit cell parameters a [Å]	14.7412(4)
b [Å]	12.0466(3)
c [Å]	13.0631(5)
β [°]	93.468(2)
V [Å^3]	2315.5(1)
D_X [g cm^{-3}]	1.362
μ(Mo$K\alpha$) [mm^{-1}]	0.429
Scan type	ϕ and ω
$2\theta_{(max)}$ [°]	50
Transmission factors (min; max)	0.886; 0.982
Total reflections measured	34345
Symmetry independent reflections	4060
Reflections with $I > 2\sigma(I)$	3162
Reflections used in refinement	4060
Parameters refined; restraints	309; 39
Final $R(F)$ [$I>2\sigma(I)$ reflections]	0.0412
$wR(F^2)$ (all data)*	0.1068
Goodness of fit	1.035
Secondary extinction coefficient	0.0026(6)
Final Δ_{max}/σ	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.64; -0.47

*$w = [\sigma^2(F_o^2) + (0.0439P)^2 + 1.8397P]^{-1}$, where $P = (F_o^2+2F_c^2)/3$

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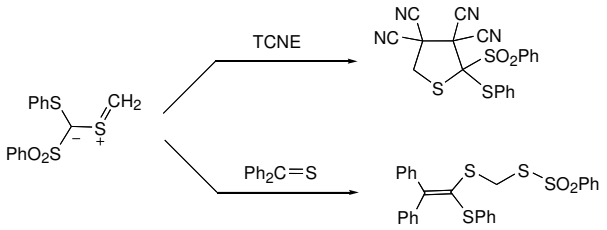
Graphical Abstract

GENERATION AND [2+3] CYCLOADDITION OF A SULFONYLATED THIOCARBONYL *S*-METHANIDE



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Cycloaddition 1,3-Dipoles Rearrangement Thiocarbonyl *S*-Methanides Thioketones